

(19)日本国特許庁 (JP)

(12) 公開特許公報 (A)

(11)特許出願公開番号

特開2000-231919

(P2000-231919A)

(43)公開日 平成12年8月22日 (2000.8.22)

(51)Int.Cl.⁷
H 01 M 4/50
4/02
4/58
// H 01 M 10/40

識別記号

F I
H 01 M 4/50
4/02
4/58
10/40

テ-マコ-ト(参考)
5 H 0 0 3
C 5 H 0 1 4
5 H 0 2 9
Z

審査請求 未請求 請求項の数 5 O L (全 10 頁)

(21)出願番号

特願平11-31091

(22)出願日

平成11年2月9日(1999.2.9)

(71)出願人 000004260

株式会社デンソー
愛知県刈谷市昭和町1丁目1番地

(71)出願人 000006183

三井金属鉱業株式会社
東京都品川区大崎1丁目11番1号

(72)発明者 鈴木 覚

愛知県刈谷市昭和町1丁目1番地 株式会
社デンソー内

(74)代理人 100081776

弁理士 大川 宏

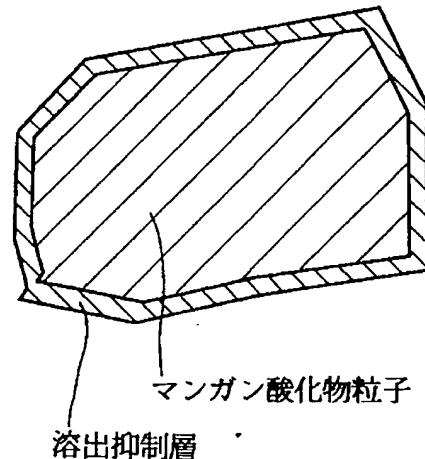
最終頁に続く

(54)【発明の名称】 正極活物質および非水電解質二次電池

(57)【要約】

【課題】 正極活物質に安価なマンガン酸化物を使用し
ていながら、高温環境下で使用されても充放電特性の劣
化が少ない非水電解質二次電池を提供すること。

【解決手段】 本発明の正極活物質は、マンガン酸化物
を主成分とするマンガン酸化物粒子と、同マンガン酸化
物粒子の表面を覆う非高分子被膜であってマンガンの溶
出を抑制する溶出抑制層とを有する。そして、本発明の
非水電解質二次電池は、前記正極活物質を正極にもつ
て、充放電時に溶出抑制層に阻まれ、非水電解質(例え
ば非水電解液)が活性の高いマンガン元素に接触しない
ので、同非水電解質がマンガンによって電気分解され
てしまうことが防止される。また、前記正極活物質からマ
ンガンが溶けだして負極に悪い作用をすることもない。
それゆえ本発明の非水電解質二次電池は、長時間に渡り
高温で保存ないし充放電されてもより大きな放電容量を
維持することができ、充放電特性の劣化が少ない。



THIS PAGE BLANK (USPTO)

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-231919

(43)Date of publication of application : 22.08.2000

(51)Int.CI. H01M 4/50

H01M 4/02

H01M 4/58

// H01M 10/40

(21)Application number : 11-031091

(71)Applicant : DENSO CORP

MITSUI MINING &
SMELTING CO LTD

(22)Date of filing : 09.02.1999

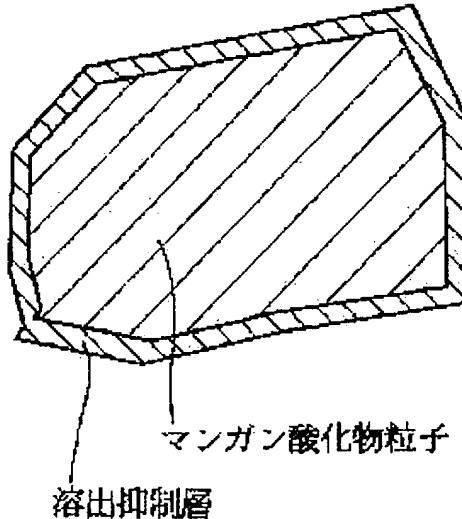
(72)Inventor : SUZUKI SATORU
NAKAMURA MASAYA
HASEGAWA JUN
NUMATA KOICHI
ISHIDA SHINTARO

(54) POSITIVE ELECTRODE ACTIVE MATERIAL AND NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a nonaqueous electrolyte secondary battery with less deteriorated charging/discharging characteristics even when used under high temperature conditions using inexpensive manganese oxides for a positive active material.

SOLUTION: This positive active material has a manganese oxide particle mainly containing a manganese oxide and an elution suppressing layer of a non-polymer film covering the manganese oxide particle for suppressing elution of a manganese. This nonaqueous electrolyte secondary battery has the positive active material in a positive electrode. A nonaqueous electrolyte (an electrolyte solution, for example) is not brought into contact with a manganese element highly active by blocking the elution suppressing layer so that the nonaqueous electrolyte is prevented from being electrolyzed by the



manganese. A negative electrode is not badly affected by eluting the manganese from the positive active material. Therefore, this nonaqueous electrolyte secondary battery can maintain large discharging capacity even if stored or charged/discharged under high temperature conditions for a long time and deterioration of charging/ discharging characteristics is reduced.

CLAIMS

[Claim(s)]

[Claim 1] Positive active material characterized by having the manganic acid ghost particle which uses a manganic acid ghost as a principal component, and the elution control layer which is a wrap non-macromolecule coat about the front face of this manganic acid ghost particle, and controls the elution of the manganese from this manganic acid ghost particle.

[Claim 2] Said elution control layer is positive active material according to claim 1 constituted considering one of lithium multiple oxides as a principal component among Ti, V, Mo, W, Co, and nickel.

[Claim 3] Said manganic acid ghost is positive active material given in either among claims 1-2 which are either among the multiple oxide of a lithium and manganese, and a manganese dioxide.

[Claim 4] The combination weight ratio of said manganic acid ghost particle and said elution control layer is positive active material given in either among claims 1-3 which are 1:0.001 thru/or 1:0.01.

[Claim 5] The nonaqueous electrolyte rechargeable battery characterized by having positive active material given in either in a positive electrode among claims 1-4.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention belongs to the technical field of the nonaqueous electrolyte rechargeable battery containing a rechargeable lithium-ion battery and a lithium secondary battery.

[0002]

[Description of the Prior Art] In recent years, development of cordless electronic equipment, such as a video camera, a portable telephone, and a pocket personal computer, is remarkable, and the nonaqueous electrolyte rechargeable battery which cell voltage can charge by the high energy consistency highly as these cells for power sources attracts attention. As positive active material used for such a nonaqueous electrolyte rechargeable battery, they are LiV₃O₈, LiCoO₂, and LiNiO₂. And use of various lithium transition-metals multiple oxides, such as LiMn₂O₄, is considered. Also in these, promising ** of the manganese system oxides, such as LiMn₂O₄, is carried out especially from the very cheap thing.

[0003] However, if a manganic acid ghost is used as positive active material, it is known that following un-arranging will arise. Since the charge electrical potential difference exceeding 4V is applied to a nonaqueous electrolyte rechargeable battery in the first place, the electrolytic solution will be disassembled by the catalysis of manganese with high activity, and un-arranging [that a cell property deteriorates] arises. The manganese which began to melt [second] from the front face of positive active material moves in

the inside of nonaqueous electrolyte, and it acts to a negative electrode, and also produces un-arranging [of checking charge and discharge]. Under hot environments, these especially un-arranging are remarkable and causes remarkable degradation of a charge-and-discharge cycle property, and degradation of a preservation property.

[0004] Then, the technique in which other transition metals permute the manganese of the front face of a spinel mold lithium manganic acid ghost is indicated by JP,9-35712,A in order to cancel first un-arranging (conventional technique 1). However, since manganese is still distributed over most front faces of a lithium manganic acid ghost depending on this technique, manganese can melt, **** cannot fully be controlled and it cannot cancel second un-arranging.

[0005] Moreover, the technique which covers positive active material with a lithium ion conductivity polymer is indicated by JP,10-125306,A for the same purpose (conventional technique 2). However, if a manganic acid ghost is used for positive active material, since the electrolytic solution will permeate the interior of a lithium ion conductivity polymer and the front face of a manganic acid ghost will be contacted also with this technique, manganese will begin to melt into nonaqueous electrolyte through covering of this polymer. So, it does not come to cancel second above-mentioned un-arranging too with the conventional technique 2.

[0006] Consequently, also with the conventional technique 1, as long as the cheap manganic acid ghost is being used for positive active material also with the conventional technique 2, if it is used under hot environments, only the nonaqueous electrolyte rechargeable battery with which a charge-and-discharge property deteriorates can be offered.

[0007]

[Problem(s) to be Solved by the Invention] Then, using the cheap manganic acid ghost for positive active material, even if this invention is used under hot environments, it makes it the technical problem which should be solved to offer a nonaqueous electrolyte rechargeable battery with little degradation of a charge-and-discharge property. Also let it be the technical problem which should be solved to offer the cheap positive active material which uses as a principal component the manganic acid ghost used for such a nonaqueous electrolyte rechargeable battery with this.

[0008]

[Means for Solving the Problem] In order to solve the above-mentioned technical problem, the artificer invented the following means.

(The 1st means) The 1st means of this invention is positive active material according to claim 1. If the positive active material of this means is used, a nonaqueous electrolyte rechargeable battery with the following advantages can be manufactured.

[0009] That is, with this means, as shown in drawing 1, it is covered with the non-macromolecule coat of an elution control layer with which manganese melts from a manganic acid ghost particle, and the front face of the manganic acid ghost particle which is the principal component of positive active material controls ****. Here, when a nonaqueous electrolyte rechargeable battery is constituted, as for an elution control layer, it is desirable not to emit manganese to nonaqueous electrolyte from the elution control layer itself not to mention the manganese from a manganic acid ghost particle to nonaqueous electrolyte melting, and controlling ****. Moreover, as for an elution control layer, it is desirable to have the property in which nonaqueous electrolyte is not made to

penetrate so that nonaqueous electrolyte may touch a manganic acid ghost particle through an elution control layer and may not denaturalize in response to an activity operation of manganese, even if the high voltage is comparatively built at the time of charge. Then, it is desirable to use the lithium system multiple oxide with which the manganese element is not contained for an elution control layer, and not to contain the manganese element in the elution control layer itself.

[0010] So, in the positive electrode of a nonaqueous electrolyte rechargeable battery, since it is prevented that nonaqueous electrolyte touches manganese with high activity directly, first un-arranging [that nonaqueous electrolyte will be decomposed by the catalysis of manganese and a cell property deteriorates by it] is avoided. Moreover, by the same reason, since the elution of the manganese from the manganic acid ghost particle of positive active material to the inside of nonaqueous electrolyte is controlled, the eluted manganese moves in the inside of nonaqueous electrolyte, it acts on a negative electrode, and second un-arranging [of checking the charge and discharge of a nonaqueous electrolyte rechargeable battery] is also prevented. Consequently, it is prevented that a cell property does not deteriorate even if it also charges first above-mentioned un-arranging by the high voltage comparatively, since second un-arranging is also canceled, but a charge-and-discharge property deteriorates even if it keeps thru/or uses it at an elevated temperature comparatively.

[0011] If the nonaqueous electrolyte rechargeable battery which only consists of a naked manganic acid ghost particle is specifically compared with the nonaqueous electrolyte rechargeable battery as one example of this invention, as shown in drawing 2 and drawing 3, the outstanding charge-and-discharge cycle property and outstanding preservation property under an elevated temperature will be proved. That is, drawing 2 is a graph which shows the fall of the discharge capacity at the time of repeating charge and discharge for the example of a comparison which does not have an elution control layer in a manganic acid ghost particle, and the nonaqueous electrolyte rechargeable battery of this invention with a predetermined elution control layer in a 60-degree C ambient atmosphere. It is clear from drawing 2 that the direction of the nonaqueous electrolyte rechargeable battery of this invention in which it has the positive active material of this means when the number of cycles exceeds about 40 excels in discharge capacity, and only the initial capacity to about 20 excels [direction / of the example of a comparison] in an elevated-temperature charge-and-discharge cycle property although the number of cycles of charge and discharge is a little excellent. In addition, it is possible to manufacture the example superior to the example of a comparison with the means of forming an elution control layer with a lithium cobalt multiple oxide also about initial capacity, so that it may mention later. On the other hand, drawing 3 is a bar graph which compares and shows the elevated-temperature preservation property of the above-mentioned example of a comparison, and one example of this invention about the recovery factor of the discharge capacity of the nonaqueous electrolyte rechargeable battery [finishing / charge] which made early discharge capacity 100% and was left in the 60-degree C ambient atmosphere for 300 hours. The discharge capacity fall according [the direction of one example of this invention] to elevated-temperature preservation is improved about several% so that clearly from drawing 3.

[0012] Therefore, according to this means, though the manganic acid ghost is used for a principal component and it is cheap, even if used under hot environments, it is effective

in the ability to offer the positive active material of a nonaqueous electrolyte rechargeable battery with little degradation of a charge-and-discharge property. Here, nonaqueous electrolyte is a concept which does not say only nonaqueous electrolyte but also contains gel nonaqueous electrolyte and solid electrolytes (polymer of a certain kind etc.), and is a concept containing an ion conductivity high medium general [equivalent to a solvent]. So, although the nonaqueous electrolyte rechargeable battery also contains the nonaqueous electrolyte rechargeable battery, it has pointed out the concept larger than a nonaqueous electrolyte rechargeable battery.

[0013] Moreover, as a manganic acid ghost, although a lithium, and the multiple oxide and manganese dioxide of manganese are typical, as long as the cell engine performance and cost allow, other manganic acid ghosts may be used. In addition, although it is most desirable to cover all front faces with the elution control layer as for a manganic acid ghost particle, even if there is a front face which is not covered in part, cycle capacity and a preservation property only fall a little. So, although there is not necessarily no need that all the front faces of a manganic acid ghost particle are covered with the elution control layer, it is desirable to cover as many parts as possible with the elution control layer among the front faces of a manganic acid ghost particle.

[0014] Furthermore, as an approach of manufacturing the positive active material of this means, there are the following approaches, for example. First, as a raw material which forms an elution control layer, a lithium raw material and metallic element raw materials other than manganese are mixed, and this mixture impalpable powder is added to a manganic acid ghost particle, and it mixes. After an appropriate time, the mixture of the mixture impalpable powder and the manganic acid ghost particle which form an elution control layer is calcined, and the positive active material of this means is obtained. As said lithium raw material, Li_2CO_3 , $\text{LiOH}\text{-H}_2\text{O}$, LiOH , etc. are mentioned here, for example. moreover -- as said metallic element raw material -- TiO_2 , V_2O_5 , and WO_3 and MoO_3 etc. -- an oxide and acids, such as H_2WO_4 and H_2MoO_4 , can be mentioned. If burning temperature is set as 500-900 degrees C, sufficient baking operation will be acquired. Moreover, as for the maintenance time amount of burning temperature, it is desirable that it is 1 - 30 hours, and it is more desirable that it is 3 - 20 hours. However, the manufacture approach of the positive active material of this means is not limited to the above approach.

[0015] (The 2nd means) The 2nd means of this invention is positive active material according to claim 2. That is, the elution control layer consists of these means considering one of lithium multiple oxides as a principal component among Ti, V, Mo, W, Co, and nickel. So, since most (or completely) Mn is not contained in an elution control layer but Mn does not begin to melt into nonaqueous electrolyte from an elution control layer, if the positive active material of this means is used for a nonaqueous electrolyte rechargeable battery, the nonaqueous electrolyte rechargeable battery can demonstrate good endurance.

[0016] In addition, about the case where Ti, V, Mo, or W is adopted, although the engine performance which excelled [example / below-mentioned / each] in the nonaqueous electrolyte rechargeable battery is clarified, also when Co or nickel is adopted, the similarly excellent cell engine performance is demonstrated. Since an elution control layer demonstrates not only the operation as an elution control layer but the operation as positive active material when Co or nickel is adopted as an elution control layer, there is

almost no fall of initial capacity like the after-mentioned, and the more excellent cell engine performance is obtained.

[0017] (The 3rd means) The 3rd means of this invention is positive active material according to claim 3. That is, with this means, a manganic acid ghost is either among the multiple oxide of a lithium and manganese, and a manganese dioxide. In the 1st above-mentioned means, although other things were employable as a manganic acid ghost, with this means, it is comparatively cheap and limitation was added from a viewpoint of an object also with easy acquisition and manufacture of a raw material. As a multiple oxide (lithium manganese multiple oxide) of a lithium and manganese, $LiMn204$, $Li1+XMn2-xO4$, $Li1+XMn2-x-yMeyO4$ (however, Me metallic elements other than Mn), etc. are employable, for example.

[0018] Therefore, according to this means, in addition to the effectiveness of the 1st above-mentioned means or the 2nd means, the effectiveness that it is comparatively cheap and acquisition and manufacture of a raw material are also easy is produced.

(The 4th means) The 4th means of this invention is positive active material according to claim 4. With this means, limitation by it being 1:0.001 thru/or 1:0.01 is added about the combination weight ratio of a manganic acid ghost particle and an elution control layer. Here, the combination weight ratio of a manganic acid ghost particle and an elution control layer interrupts 1:0.001, if small, under hot environments, the elution depressant action of the manganese of an elution control layer will become small, and the preservation property of the nonaqueous electrolyte rechargeable battery under an elevated temperature will deteriorate. Conversely, if this combination weight ratio is large exceeding 1:0.01, it will produce un-arranging [that the coat of an elution control layer becomes thick, the electric resistance which this coat has becomes large, and the internal resistance of a nonaqueous electrolyte rechargeable battery increases].

Therefore, if the range of a combination weight ratio is limited like this means, while degradation of the preservation property under the elevated temperature of a nonaqueous electrolyte rechargeable battery is prevented effectively, the internal resistance of a nonaqueous electrolyte rechargeable battery also seldom needs to become large.

Consequently, the nonaqueous electrolyte rechargeable battery which is durable also under an elevated temperature can be offered, without reducing the initial engine performance of a nonaqueous electrolyte rechargeable battery not much.

[0019] Therefore, according to this means, it is effective in the ability to manufacture now the nonaqueous electrolyte rechargeable battery with which initial performance degradation is durable also under an elevated temperature few in addition to the effectiveness of the 1st above-mentioned means thru/or the 3rd means.

(The 5th means) The 5th means of this invention is a nonaqueous electrolyte rechargeable battery according to claim 5.

[0020] That is, with this means, since it is characterized by having one of positive active material in a positive electrode among the 1st above-mentioned means thru/or the 4th means, either is demonstrated among the effectiveness which each means has. That is, using the manganic acid ghost cheap as a principal component of positive active material, even if used under hot environments, it becomes possible to offer a nonaqueous electrolyte rechargeable battery with little degradation of a charge-and-discharge property.

[0021] Therefore, according to the nonaqueous electrolyte rechargeable battery of this

means, though it is cheap, the initial engine performance seldom falls but it is effective in the ability to demonstrate the endurance excellent also in the long-term use under an elevated temperature. In addition, as a negative-electrode active material of the nonaqueous electrolyte rechargeable battery of this means, occlusion and various kinds of matter which can be emitted are [the lithium ion other than a lithium metal or a lithium alloy] electrochemically employable. for example, carbon system ingredients, such as a graphite, corks, and an organic high molecular compound, and positive active material -- comparing -- SnO and TiO₂ with low potential etc. -- a metallic oxide etc. is employable. [0022] Moreover, as nonaqueous electrolyte of the nonaqueous electrolyte rechargeable battery of this means, although not limited to nonaqueous electrolyte as mentioned above, the nonaqueous electrolyte which lithium salt was used [nonaqueous electrolyte] as the supporting electrolyte and dissolved this supporting electrolyte in various kinds of organic solvents is typical. here -- as a supporting electrolyte -- LiClO₄, LiBF₄, LiPF₆, and LiCF₃ -- SO₃, LiN(CF₃SO₂)₂, LiN(C₂F₅SO₂)₂, LiN(CF₃SO₂)(C₄F₉SO₂), etc. are employable. Since the manganese from the positive active material by the fluoric acid which separated melts in the nonaqueous electrolyte in which the supporting electrolyte containing a fluorine was contained and *** is effectively prevented by the elution control layer also in these, the effectiveness which this means has is demonstrated remarkably. On the other hand, as an organic solvent of nonaqueous electrolyte, propylene carbonate, ethylene carbonate, 1, 2-dimethoxyethane, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, a tetrahydrofuran, 2-methyl tetrahydrofuran, tetrahydropyran, etc. are employable, for example. In the nonaqueous electrolyte which contains the organic solvent of a carbonate system also in these, since charge and discharge are comparatively performed by the high voltage, the effectiveness of the nonaqueous electrolyte rechargeable battery of this means without the thing beyond 4V for which manganese touches nonaqueous electrolyte with almost among positive active material shows up notably.

[0023]

[Embodiment of the Invention] clear [contrasting the example and the example of a comparison of a nonaqueous electrolyte rechargeable battery which have the positive active material of this invention in a positive electrode so that an understanding which can be carried out to this contractor may be acquired] about the gestalt of operation of the positive active material of this invention, and a nonaqueous electrolyte rechargeable battery -- and it fully explains.

[Example]

(Example 1:A1) The nonaqueous electrolyte rechargeable battery which has the positive active material and this positive active material as an example 1 of this invention in a positive electrode was prepared as follows.

[0024] That is, it is TiO₂ of 19.9g of Li₂CO₃ and 86.3g first. It mixed uniformly with the mortar and the mixture (mixture 1) of Li/Ti=1/2 was created by the mole ratio. Subsequently, 1.8kg Li_{1.12}Mn_{1.88}O₄ beforehand calcinated and prepared at 900 degrees C It mixed until it received, it added only 10.6g of mixture 1 and it became uniform with the mortar further, and new mixture (mixture 2) was obtained. and the result which threw mixture 2 into the crucible made from an alumina, and was calcinated over 20 hours at the temperature of 650 degrees C in air -- Li_{1.12}Mn_{1.88}O₄ from -- the becoming manganic acid ghost particle and the elution control layer which is the coat

which consists the front face of a wrap lithium titanium multiple oxide were formed. In addition, Li_{1.12}Mn_{1.88}O₄ at this time The combination weight ratio with the combination weight ratio of the lithium titanium multiple oxide to receive, i.e., a manganic acid ghost, and an elution control layer is 1:0.005 (0.5 % of the weight).

[0025] Consequently, the positive active material which consists of a manganic acid ghost particle which uses a manganic acid ghost as a principal component, and an elution control layer which is a wrap non-macromolecule coat about the front face of this manganic acid ghost, and controls the elution of the manganese from this manganic acid ghost particle was manufactured. Here, a manganic acid ghost is the oxide of an almost pure lithium and manganese, and, on the other hand, an elution control layer is an almost pure lithium titanium multiple oxide, i.e., a lithium multiple oxide with Ti. Moreover, the value of 1:0.005 of the combination weight ratio of a manganic acid ghost and an elution control layer is equivalent to the in-between value of the range of 1:0.001 thru/or 1:0.01. [0026] In addition, the diameter of a manganic acid ghost particle is 4 micrometers about among this positive active material, and if the thickness of the elution control layer which has covered the front face of this particle is 0.003-0.01 micrometers in general, it will be presumed on count. Moreover, although it is a guess to the last, it is thought from height called 88% of a capacity maintenance factor that the elution control layer has covered most front faces of a manganic acid ghost particle.

[0027] The nonaqueous electrolyte rechargeable battery which has said positive active material in a positive electrode was created as follows in order to check the effectiveness of the positive active material of this example. The positive electrode was begun from the production of a paste which contains positive active material first. That is, the positive active material of 86% of the weight of this example, 10% of the weight of the graphite as electric conduction material, and 4% of the weight of PVDF (polyvinylidene fluoride) as a binder were melted in the N-methyl-2-pyrrolidone as a solvent, and the paste was created. After an appropriate time, this paste was uniformly applied to one front face of the charge collector which consists of aluminium foil by predetermined weight and thickness, and the aluminium foil with which positive active material was held on the surface of one side after desiccation of this paste was pierced to discoid with a diameter of 14mm. And after carrying out pressing of the positive active material held on the surface of aluminium foil and compressing it a little, the positive electrode was created by carrying out a vacuum drying.

[0028] On the other hand, the negative electrode pierced the metal lithium foil of predetermined thickness to discoid with a diameter of 15mm, and was created. Moreover, the nonaqueous electrolyte as nonaqueous electrolyte is LiPF₆ as an electrolyte which is a solute at the mixed solution of the ethylene carbonate and diethyl carbonate which were mixed by the volume ratio 3:7. It was adjusted by melting at a rate of one mol/l. In addition, as a separator, thickness adopted the porous membrane made from polyethylene whose void content is 40% by 25 micrometers.

[0029] And the diameter of a container created the nonaqueous electrolyte rechargeable battery A1 of an assembly and an example 1 for the nonaqueous electrolyte rechargeable battery of flat this invention whose thickness is 3.0mm by 20mm using the positive electrode, the negative electrode, and nonaqueous electrolyte which were created as mentioned above. As the major characteristics of the nonaqueous electrolyte rechargeable battery A1 of an example 1 are shown in the next table 1, the coat of an elution control

layer is formed with the lithium multiple oxide with Ti, and the weight ratio of an elution control layer to a manganic acid ghost particle is 1:0.005 (0.5 % of the weight). Moreover, the initial discharge capacity per [to the example B9 of a comparison which created the naked manganic acid ghost as positive active material like the after-mentioned] unit weight was 97%. Furthermore, as a result of performing a charge-and-discharge cycle trial, the capacity maintenance factor to this initial discharge capacity is 0.88 (88%), and marked the value higher than any among each below-mentioned example of a comparison. In addition, the charge-and-discharge cycle trial is performed on the same conditions by each example and each example of a comparison. That is, it sets to the 60-degree C hot environments in a thermostat, and a charge-and-discharge cycle trial is charging current consistency 0.5 mA/cm². Discharge current consistency 0.5 mA/cm² after charging to 4.3V The trial process which discharges to 3V was performed as 1 cycle. And the value which broke the discharge capacity in 50 cycle eye by initial discharge capacity was indicated to Table 1 as a capacity maintenance factor of the nonaqueous electrolyte rechargeable battery.

[0030]

[Table 1]

電池	被膜を形成する元素	被膜のリチウムマンガン酸化物に対する重量比(wt%)	重量あたりの初期容量(電池B9の容量を100とする)	容量維持率
A1	Ti	0.5	97	0.88
A2	V	0.5	95	0.86
A3	W	0.5	96	0.87
A4	Mo	0.5	96	0.87
A5	Ti	0.1	98	0.82
A6	Ti	1	97	0.90
A7	V	0.1	96	0.79
A8	V	1	94	0.88
A9	W	0.1	97	0.80
A10	W	1	95	0.88
A11	Mo	0.1	97	0.80
A12	Mo	1	95	0.88
A13	Ti	0.5	97	0.88
A14	W	0.5	95	0.87
A15	Mo	0.5	95	0.87
B1	Ti	0.05	98	0.76
B2	Ti	5	90	0.79
B3	V	0.05	96	0.74
B4	V	5	90	0.78
B5	W	0.05	97	0.75
B6	W	5	87	0.78
B7	Mo	0.05	97	0.75
B8	Mo	5	87	0.78
B9	なし	0	100	0.74

[0031] (Example 2:A2) An example 2 is TiO₂ as one side of the starting material of an elution control layer. Except for the point which replaced with and used V₂O₅, it is the same as that of an example 1. That is, in this example, V₂O₅ of 19.2g of Li₂CO₃ and

94.7g were uniformly mixed with the mortar, and the mixture (mixture 1) of Li/V=1/2 was created by the mole ratio like the example 1. Subsequently, 1.8kg Li1.12Mn 1.88O4 beforehand calcinated and prepared at 900 degrees C It received, it mixed until it added only 11.4g of mixture 1 and became uniform with the mortar further, and new mixture (mixture 2) was obtained. and the result which threw mixture 2 into the crucible made from an alumina, and was calcinated over 20 hours at the temperature of 650 degrees C in air -- Li1.12Mn 1.88O4 from -- the becoming manganic acid ghost particle and the elution control layer which is the coat which consists the front face of a wrap lithium vanadium multiple oxide were formed. In addition, Li1.12Mn 1.88O4 at this time The combination weight ratio with the combination weight ratio of the lithium vanadium multiple oxide to receive, i.e., a manganic acid ghost, and an elution control layer is the 1:0.005 [same] (0.5 % of the weight) as an example 1.

[0032] Moreover, if the point which has adopted the above positive active material is removed, the approach of beginning the approach of creating a positive electrode and creating the nonaqueous electrolyte rechargeable battery A2 of an example 2 is the same as that of an example 1. Furthermore, initial discharge capacity and a capacity maintenance factor were also measured with the same test method as an example 1.

Consequently, as shown in said table 1, the initial capacity per unit weight has only been 95% fewer about 2% than the above-mentioned example 1. Moreover, the capacity maintenance factor of 50 cycle eye in a charge-and-discharge cycle trial is also 0.87 only with less 0.01 than an example 1. However, the capacity maintenance factor of this example has also marked the value higher than any of each below-mentioned example of a comparison.

[0033] (Example 3:A3) An example 3 is TiO2 as one side of the starting material of an elution control layer. Except for the point which replaced with and used H2WO4, it is the same as that of an example 1. That is, in this example, H2WO4 of 13.9g of Li2CO3 and 94.2g was uniformly mixed with the mortar, it differed in the example 1, and the mixture (mixture 1) of Li/W=1/1 was created by the mole ratio. Subsequently, 1.8kg Li1.12Mn 1.88O4 beforehand calcinated and prepared at 900 degrees C It received, it mixed until it added only 10.8g of mixture 1 and became uniform with the mortar further, and new mixture (mixture 2) was obtained. and the result which threw mixture 2 into the crucible made from an alumina, and was calcinated over 20 hours at the temperature of 650 degrees C in air -- Li1.12Mn 1.88O4 from -- the becoming manganic acid ghost particle and the elution control layer which is the coat which consists the front face of a wrap lithium tungsten multiple oxide were formed. In addition, Li1.12Mn 1.88O4 at this time The combination weight ratio with the combination weight ratio of the lithium tungsten multiple oxide to receive, i.e., a manganic acid ghost, and an elution control layer is the 1:0.005 [same] (0.5 % of the weight) as an example 1.

[0034] Moreover, if the point which has adopted the above positive active material is removed, the approach of beginning the approach of creating a positive electrode and creating nonaqueous electrolyte rechargeable battery A3 of an example 3 is the same as that of an example 1. Furthermore, initial discharge capacity and a capacity maintenance factor were also measured with the same test method as an example 1. Consequently, as shown in said table 1, the initial capacity per unit weight has only been 96% fewer about 1% than the above-mentioned example 1. Moreover, the capacity maintenance factor of 50 cycle eye in a charge-and-discharge cycle trial is also 0.87 only with less 0.01 than an

example 1. However, the capacity maintenance factor of this example has also marked the value higher than any of each below-mentioned example of a comparison.

[0035] (Example 4:A4) An example 4 is TiO_2 as one side of the starting material of an elution control layer. It replaces with and is MoO_3 . Except for the used point, it is the same as that of an example 1. That is, at this example, it is MoO_3 of 22.0g of Li_2CO_3 3 and 85.9g. It mixed uniformly with the mortar, it differed in the example 1, and the mixture (mixture 1) of $Li/Mo=1/1$ was created by the mole ratio. Subsequently, 1.8kg $Li_{1.12}Mn_{1.88}O_4$ beforehand calcinated and prepared at 900 degrees C It received, it mixed until it added only 10.8g of mixture 1 and became uniform with the mortar further, and new mixture (mixture 2) was obtained. and the result which threw mixture 2 into the crucible made from an alumina, and was calcinated over 20 hours at the temperature of 650 degrees C in air -- $Li_{1.12}Mn_{1.88}O_4$ from -- the becoming manganic acid ghost particle and the elution control layer which is the coat which consists the front face of a wrap lithium molybdenum multiple oxide were formed. In addition, $Li_{1.12}Mn_{1.88}O_4$ at this time The combination weight ratio with the combination weight ratio of the lithium molybdenum multiple oxide to receive, i.e., a manganic acid ghost, and an elution control layer is the 1:0.005 [same] (0.5 % of the weight) as an example 1.

[0036] Moreover, if the point which has adopted the above positive active material is removed, the approach of beginning the approach of creating a positive electrode and creating nonaqueous electrolyte rechargeable battery A4 of an example 4 is the same as that of an example 1. Furthermore, initial discharge capacity and a capacity maintenance factor were also measured with the same test method as an example 1. Consequently, as shown in said table 1, the initial capacity per unit weight has only been 96% fewer about 1% than the above-mentioned example 1. Moreover, the capacity maintenance factor of 50 cycle eye in a charge-and-discharge cycle trial is also 0.87 only with less 0.01 than an example 1. However, the capacity maintenance factor of this example has also marked the value higher than any of each below-mentioned example of a comparison.

[0037] (Example 5-12:A5-A12) The front face of a lithium manganic acid ghost was covered, and the coat of the elution control layer which consists of a lithium multiple oxide with Ti , V , W , or Mo like examples 1-4 was formed. And lithium manganic acid ghost $Li_{1.12}Mn_{1.88}O_4$ of this coat The receiving weight ratio was mixed by 1:0.001 (0.1 % of the weight) or 1:0.01 (1 % of the weight), as shown in said table 1, and the positive active material of each example was created. These two kinds of mixed weight ratios are the lower limits and upper limits of the range of 1:0.001 which is a desirable mixed weight ratio thru/or 1:0.01.

[0038] Moreover, the examples 5-12 (A5-A12) of the nonaqueous electrolyte rechargeable battery which has the positive electrode which carried out pressing of each positive active material etc. like an example 1 in one front face of the charge collector which consists of aluminium foil were created. The term of the below-mentioned comparative evaluation explains evaluation of these examples.

(Example 13:A13) The point which replaced the positive active material of this example with one side of the starting material for forming an elution control layer at Li_2CO_3 , and adopted $LiOH$ differs from the example 1.

[0039] That is, at this example, they are 12.9g $LiOH$ and 86.3g TiO_2 . It mixed uniformly with the mortar, it differed in the example 1, and the mixture (mixture 1) of $Li/Ti=1/1$ was created by the mole ratio. Subsequently, 1.8kg $Li_{1.12}Mn_{1.88}O_4$ beforehand

calcinated and prepared at 900 degrees C It received, it mixed until it added only 9.92g of mixture 1 and became uniform with the mortar further, and new mixture (mixture 2) was obtained. and the result which threw mixture 2 into the crucible made from an alumina, and was calcinated over 20 hours at the temperature of 650 degrees C in air -- Li1.12Mn 1.88O4 from -- the becoming manganic acid ghost particle and the elution control layer which is the coat which consists the front face of a wrap lithium titanium multiple oxide were formed. In addition, Li1.12Mn 1.88O4 at this time The combination weight ratio with the combination weight ratio of the lithium titanium multiple oxide to receive, i.e., a manganic acid ghost, and an elution control layer is the 1:0.005 [same] (0.5 % of the weight) as an example 1.

[0040] Moreover, the approach of beginning the approach of creating a positive electrode and creating the nonaqueous electrolyte rechargeable battery A13 of an example 13 is the same as that of an example 1. Furthermore, initial discharge capacity and a capacity maintenance factor were also measured with the same test method as an example 1. The term of the below-mentioned comparative evaluation also explains evaluation of this example (A13).

(Example 14:A14) It differs from the example 3 in that the positive active material of this example adopted LiOH as one side of the starting material for forming an elution control layer.

[0041] That is, at this example, they are 16.4g LiOH and 79.7g WO₃. It mixed uniformly with the mortar, it differed in the example 3, and the mixture (mixture 1) of Li/W=2/1 was created by the mole ratio. Subsequently, 1.8kg Li1.12Mn 1.88O4 beforehand calcinated and prepared at 900 degrees C It received, it mixed until it added only 9.61g of mixture 1 and became uniform with the mortar further, and new mixture (mixture 2) was obtained. and the result which threw mixture 2 into the crucible made from an alumina, and was calcinated over 20 hours at the temperature of 650 degrees C in air -- Li1.12Mn 1.88O4 from -- the becoming manganic acid ghost particle and the elution control layer which is the coat which consists the front face of a wrap lithium tungsten multiple oxide were formed. In addition, Li1.12Mn 1.88O4 at this time The combination weight ratio with the combination weight ratio of the lithium tungsten multiple oxide to receive, i.e., a manganic acid ghost, and an elution control layer is the 1:0.005 [same] (0.5 % of the weight) as an example 3.

[0042] Moreover, the approach of beginning the approach of creating a positive electrode and creating the nonaqueous electrolyte rechargeable battery A14 of an example 14 is the same as that of an example 1. Furthermore, initial discharge capacity and a capacity maintenance factor were also measured with the same test method as an example 1. The term of the below-mentioned comparative evaluation also explains evaluation of this example (A14).

(Example 15:A15) It differs from the example 4 in that the positive active material of this example adopted LiOH as one side of the starting material for forming an elution control layer.

[0043] That is, at this example, they are 24.8g LiOH and 74.5g MoO₃. It mixed uniformly with the mortar, it differed in the example 4, and the mixture (mixture 1) of Li/Mo=2/1 was created by the mole ratio. Subsequently, 1.8kg Li1.12Mn 1.88O4 beforehand calcinated and prepared at 900 degrees C It received, it mixed until it added only 9.93g of mixture 1 and became uniform with the mortar further, and new mixture

(mixture 2) was obtained. and the result which threw mixture 2 into the crucible made from an alumina, and was calcinated over 20 hours at the temperature of 650 degrees C in air -- $\text{Li}_{1.12}\text{Mn}_{1.88}\text{O}_4$ from -- the becoming manganic acid ghost particle and the elution control layer which is the coat which consists the front face of a wrap lithium molybdenum multiple oxide were formed. In addition, $\text{Li}_{1.12}\text{Mn}_{1.88}\text{O}_4$ at this time The combination weight ratio with the combination weight ratio of the lithium molybdenum multiple oxide to receive, i.e., a manganic acid ghost, and an elution control layer is the 1:0.005 [same] (0.5 % of the weight) as an example 4.

[0044] Moreover, the approach of beginning the approach of creating a positive electrode and creating the nonaqueous electrolyte rechargeable battery A15 of an example 15 is the same as that of an example 1. Furthermore, initial discharge capacity and a capacity maintenance factor were also measured with the same test method as an example 1. The term of the below-mentioned comparative evaluation also explains evaluation of this example (A15).

[The example of a comparison]

(Example of comparison 1-8:B1-B8) With the positive active material of the examples 1-8 of a comparison, it is $\text{Li}_{1.12}\text{Mn}_{1.88}\text{O}_4$ in a manganic acid ghost particle like each above-mentioned example. It was adopted. Similarly, the oxide containing Li_2CO_3 and four sorts of metallic elements corresponding to examples 1-4 etc. is adopted as the starting material of an elution control layer, and the elution control layer which consists of a lithium system multiple oxide is formed in it. However, as shown in said table 1, the weight ratio of an elution control layer to a manganic acid ghost particle is separated from it and set up from the desirable range (0.1 - 1 % of the weight), and is 0.05 % of the weight or 5 % of the weight. The positive active material of the examples 1-8 of a comparison was manufactured on such conditions. In addition, since it is satisfied only with such positive active material having not satisfied the conditions of the 4th above-mentioned means of the conditions of the 1st means thru/or the 3rd means, it should treat as an example essentially. However, since inferiority carried out the examples 1-8 of a comparison rather as compared with each above-mentioned example with which are satisfied of the conditions of the 4th means, they were made to dare treat as an example of a comparison.

[0045] Moreover, the approach of beginning the approach of creating a positive electrode and creating the nonaqueous electrolyte rechargeable batteries B1-B8 of the examples 1-8 of a comparison is the same as that of an example 1. Furthermore, initial discharge capacity and a capacity maintenance factor were also measured with the same test method as an example 1. The term of the below-mentioned comparative evaluation also explains evaluation of each of these examples of a comparison (B1-B8).

(Example of comparison 9:B9) The positive active material of this example of a comparison is $\text{Li}_{1.12}\text{Mn}_{1.88}\text{O}_4$ in a manganic acid ghost particle like each above-mentioned example and each example of a comparison. Although adopted, the wrap elution control layer does not have the front face of a manganic acid ghost particle. That is, the positive active material of this example of a comparison is not the example of this invention but the conventional technique thru/or the thing of a kind which should also usually be called technique also in strict semantics. In addition, it was created by the approach as each example of the above-mentioned [after], and each example of a comparison that the nonaqueous electrolyte rechargeable battery B9 of this example of a

comparison is also the same only by positive active material differing.

[0046] The initial discharge capacity of each example shown in said table 1 and each example of a comparison is the value compared considering the initial discharge capacity of the nonaqueous electrolyte rechargeable battery B9 of this example of a comparison as 100% of a reference value. However, the capacity maintenance factor in a charge-and-discharge cycle trial is the value which set each initial discharge capacity to 1, and was calculated by each in each example and each example of a comparison.

When X diffraction measurement was carried out to the positive active material of each example more than [comparison examination], and each example of a comparison, the difference in change of a peak pattern, the shift of a peak location, etc. was not mutually seen about the positive active material of all examples. namely, all the example and examples 1-8 of a comparison -- setting -- Li1.12Mn 1.88O4 of the example 9 of a comparison from -- the same peak pattern as a case and peak location of the positive active material of only the becoming manganic acid ghost particle were obtained. So, Li1.12Mn 1.88O4 used as the nucleus of positive active material That by which the front face of a manganic acid ghost particle is covered with the coat of the elution control layer which a structural change does not have in a manganic acid ghost particle, and consists of a lithium multiple oxide with each only added element can be presumed. If said table 1 is again improved based on the result of such X diffraction measurement, it is possible that the difference of the engine performance of each nonaqueous electrolyte rechargeable battery is produced by the difference in the elution control layer adhering to the front face of a manganic acid ghost particle.

[0047] That is, if each nonaqueous electrolyte rechargeable battery (A1 - A4) of examples 1-4 is compared mutually and examined, the nonaqueous electrolyte rechargeable battery A1 which adopted positive active material with the elution control layer of a lithium titanium multiple oxide will demonstrate the most excellent engine performance. That is, in the nonaqueous electrolyte rechargeable battery A1, it is 97% of B9 from which initial discharge capacity serves as criteria, and the capacity maintenance factor as a result of a charge-and-discharge cycle trial in an elevated-temperature ambient atmosphere is 88% of initial discharge capacity. That is, also by the result of a charge-and-discharge cycle trial in an elevated-temperature ambient atmosphere, compared with the initial discharge capacity of B9, $97\% \times 88\% = 85\%$ discharge capacity is maintained, and 74% which is the capacity maintenance factor of B9 is exceeded no less than 11%.

[0048] Therefore, according to the nonaqueous electrolyte rechargeable battery A1 of an example 1, using the cheap manganic acid ghost for the principal component of positive active material, even if used under hot environments, it is effective in degradation of a charge-and-discharge property decreasing. The engine performance is most inferior in A2 which formed the elution control layer by the lithium banazin san ghost among the nonaqueous electrolyte rechargeable battery A1 of examples 1-4 - A4. Although just initial discharge capacity is inferior in the nonaqueous electrolyte rechargeable battery A2 with 95% of B9, the capacity maintenance factor after the trial of a charge-and-discharge cycle trial has still marked 86%. So, rather than $95\% \times 86\% = 82\%$ and 74% of capacity maintenance factors of B9, discharge capacity with no less than 8 high% was maintained, and, as for the nonaqueous electrolyte rechargeable battery A2, it was proved that the charge-and-discharge cycle property under an elevated temperature is superior to the example 9 of a comparison used as criteria.

[0049] Moreover, nonaqueous electrolyte rechargeable battery A3 of the example 3 which used a tungsten and molybdenum as an alloying element of an elution control layer, respectively, and an example 4, and A4 have the equivalent engine performance mutually. That is, each of nonaqueous electrolyte rechargeable battery A3 and initial discharge capacity of A4 is 96% of B9, and each capacity maintenance factor in a charge-and-discharge cycle trial is 87%. Therefore, nonaqueous electrolyte rechargeable battery A3 of an example 3 and an example 4 and A4 demonstrate the in-between engine performance of the nonaqueous electrolyte rechargeable battery A1 of an example 1, and the nonaqueous electrolyte rechargeable battery A2 of an example 2, and the charge-and-discharge cycle property under an elevated temperature is superior to the example 9 of a comparison used as criteria too.

[0050] It became clear that Ti is most excellent among Ti, V, W, and Mo as an element added to the lithium multiple oxide which forms an elution control layer, and the charge-and-discharge cycle property under an elevated temperature is extremely excellent from the above examination. Next, the weight ratio of an elution control layer to a manganic acid ghost particle compared mutually nonaqueous electrolyte rechargeable battery A5 which is 0.1%, 0.5%, and 1%, respectively, and A1 and A6. Then, it became clear that initial discharge capacity has the one where the weight ratio of an elution control layer is lower in a high inclination. However, it became clear that the capacity maintenance factor in a charge-and-discharge cycle trial is in the inclination for the one where the weight ratio of an elution control layer is conversely higher to be high. If it considers from the above thing, what has many front faces of the manganic acid ghost particle which the thickness of an elution control layer runs short of the weight ratios of an elution control layer at 0.1 % of the weight, or is not covered with an elution control layer will be conjectured. Consequently, it has a property with the weight ratio of the elution control layer of positive active material comparatively near the nonaqueous electrolyte rechargeable battery B9 of the example 9 of a comparison with which 0.1% of the weight of nonaqueous electrolyte rechargeable battery A5 uses as positive active material the manganic acid ghost particle which consists of a naked manganese lithium oxide.

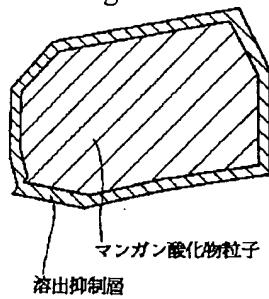
[0051] On the other hand, the maintained discharge capacity in a charge-and-discharge cycle trial makes initial discharge capacity of B9 100%, and is 80%, 85%, and 87% about nonaqueous electrolyte rechargeable battery A5, and A1 and A6, respectively. Therefore, when the weight ratios of an elution control layer were 0.1 % of the weight thru/or 1 % of the weight, it became clear to the initial discharge capacity of B9 that the discharge capacity of the base of 80% is demonstrated also for a charge-and-discharge cycle trial. Moreover, when the weight ratio of an elution control layer was 0.1 % of the weight thru/or 1% of the weight of the range, the results of 50 charge-and-discharge cycle trials were excellent, so that the weight ratio of an elution control layer was large. However, like nonaqueous electrolyte rechargeable battery B-2 of the example 2 of a comparison, if there is a weight ratio of an elution control layer also 5% of the weight, the results of 50 charge-and-discharge cycle trials will fall conversely, but good results may be obtained if a charge-and-discharge cycle trial is further performed over a long period of time. Moreover, since a capacity maintenance factor will become low like the nonaqueous electrolyte rechargeable battery B1 of the example 1 of a comparison although initial discharge capacity is high if the weight ratio of an elution control layer does not pass to 0.05% of the weight, although it is not suitable for long-term use under hot environments,

good results can be demonstrated rather than B9. So, it is thought that a proper value will become settled naturally about the weight ratio of an elution control layer to a manganic acid ghost particle if it becomes settled about the service temperature and the charge-and-discharge cycle life which are required of a nonaqueous electrolyte rechargeable battery, and it is *****.

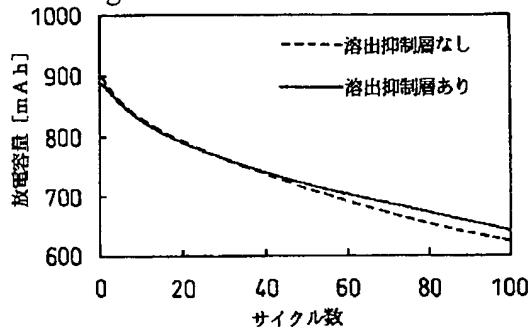
[0052] Even if it compares mutually the nonaqueous electrolyte rechargeable batteries B3, A7, A2, and A8 which similarly have the positive active material which formed the elution control layer with the lithium vanadium multiple oxide, and B4, the same inclination as the above-mentioned B1, A5, A1 and A6, and B-2 is seen. Moreover, the same inclination is accepted even if it compares mutually nonaqueous electrolyte rechargeable battery B5, A9 and A3 with the positive active material which formed the elution control layer with the lithium tungsten multiple oxide, A10, and B6. Furthermore, the same inclination is accepted even if it compares mutually the nonaqueous electrolyte rechargeable batteries B7 and A11 with the positive active material which formed the elution control layer with the lithium molybdenum multiple oxide, A4, and A12 and B8.

[0053] In addition, even if the mole ratios of the alloying element of a lithium multiple oxide and lithium element which form an elution control layer [the above-mentioned examples 1, 3, and 4 / respectively] differ examples 13-15, it turns out that there is no fluctuation large in a cell property. Therefore, the nonaqueous electrolyte rechargeable battery which has the positive active material of this invention in a positive electrode is effective in the ability to demonstrate a bigger discharge capacity in the long-term use under hot environments compared with the nonaqueous electrolyte rechargeable battery which uses a naked manganic acid ghost particle as positive active material.

Drawing 1



Drawing 2



Drawing 3

